

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : D06N 7/00, D06M 15/41	A1	(11) International Publication Number: WO 91/19849 (43) International Publication Date: 26 December 1991 (26.12.91)
(21) International Application Number: PCT/US91/03969 (22) International Filing Date: 11 June 1991 (11.06.91) (30) Priority data: 536,791 12 June 1990 (12.06.90) US (60) Parent Application or Grant (63) Related by Continuation US 536,791 (CIP) Filed on 12 June 1990 (12.06.90) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).		(72) Inventor; and (75) Inventor/Applicant (for US only) : VINOD, Yashavant, Vinayak [IN/US]; 6 Farm House Circle, Hockessin, DE 19707 (US). (74) Agents: CAPLAN, Mark, J. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: STAIN-RESISTANT FABRICS (57) Abstract <p>Fabrics, such as carpets, comprising a primary backing and tufts, which are loops and/or cut loops of nylon filaments of fiber blends containing such filaments, the tufts adhered to the primary backing by means of an adhesive are disclosed. The filaments are coated with a stain-resist composition and the adhesive contains a stain-resist composition which may or may not be the same as the stain-resist composition applied directly to the nylon filaments. Suitable stain-resist compositions include those containing condensation products of formaldehyde and sulfonated phenol or sulfonated naphthols, and addition polymers of methacrylic acid or maleic anhydride (which can be hydrolyzed to maleic acid and, if desired, isomerized to fumaric acid) and up to 70 weight percent of another monomer having ethylenic unsaturation and containing 2 to 20 carbon atoms. Blends of the condensate stain-resist composition and addition polymer stain-resist compositions may be used. Optionally, a soil-resist composition such as a fluorocarbon may also be used in the adhesive in combination with the stain-resist composition. The fabrics exhibit improved stain-resistance after washing compared with similar fabrics in which the stain-resist composition is applied to the nylon filaments and is not present in the adhesive.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

TITLE

STAIN-RESISTANT FABRICS

BACKGROUND OF THE INVENTION5 FIELD OF THE INVENTION

The present invention relates to stain-resistant carpets having improved afterwash stain performance. More particularly, it relates to a technique for improving the afterwash stain performance of stain-resistant polyamide or
10 polyamide-blend carpets by incorporating a stainblocker into the adhesive that is used to anchor the yarn tufts into the primary backing.

PRIOR ART

Polyamide substrates, such as carpeting,
15 upholstery, fabric and the like, are subject to staining by a variety of foodstuffs containing acid-dye colorants. The treatment of polyamide substrates with acid-dye-resist, levelling, or wet-fastness agents in order to render them resistant to staining by acid dyestuffs, including food
20 dyes such as FD&C Red Dye No. 40, is well known in the art.

Stain-resist agents comprising sulfonated naphthol- or sulfonated phenol-formaldehyde condensation products and methods for treating polyamide carpets or carpet yarn with these compositions to render the carpets
25 resistant to staining by acid dyes are disclosed in Ucci and Blyth U.S. Patent No. 4,501,591, Blyth and Ucci U.S. Patent No. 4,592,940, Blyth and Ucci U.S. Patent No. 4,680,212, and Greschler, Malone, and Zinnato U.S. Patent No. 4,780,099.

30 Stain-resist compositions comprising mixtures of sulfonated phenol-formaldehyde condensation products with a hydrolyzed polymer of maleic anhydride and one or more ethylenically unsaturated aromatic monomers are described
35 in Fitzgerald, Rao, Vinod, and Alender, U.S. Patent No.

4,883,839. Processes for applying these stain-resist compositions are described in Fitzgerald, et. al. in their
5 pending application Serial No. 07/280,404 which is a divisional application of the above-mentioned patent. Polyamide substrates made stain resistant by such compositions are the subject of another divisional application, Serial No. 07/280,405. An alternate process
10 for applying these stain-resist compositions is disclosed in Fitzgerald, Materniak, Moores, Openstone, and Rivet in their pending application Serial No. 07/389,894.

Olson, Chang, and Muggli, U.S. Patent No. 4,822,373 discloses treatment of fibrous polyamide
15 substrates to render them resistant to staining by acid dyestuffs by applying thereto (a) a partially sulfonated novolak resin and (b) polymethacrylic acid, copolymers of methacrylic acid, or combinations of polymethacrylic acid and copolymers of methacrylic acid.

20 Chang, Olson, and Muggli, EPO Published Application 332,342 discloses a method for imparting stain resistance to fibrous polyamide materials that involves contacting the materials with an aqueous solution comprising polymethacrylic acid, copolymers of methacrylic
25 acid, or combinations thereof.

Blyth and Ucci, U.S. Patent No. 4,619,853 discloses polyamide carpets comprising a primary backing and a pile coated with a sufficient amount of sulfonated phenol- or naphthol-formaldehyde condensation product to
30 render the carpet stain resistant, wherein the underside of the primary backing is coated with a carpet backing adhesive composition containing a fluorochemical in an amount sufficient to render the primary backing
35 substantially impervious to water. Ucci, U.S. Patent No. 4,579,762 discloses similar carpets wherein the carpet

fibers are shaped from nylon 6,6 or nylon 6 polymer modified to contain as an integral part of its polymer chain aromatic sulfonate units in an amount sufficient to
5 improve the acid dye-resist properties of the fibers. The fluorochemical which is added to the carpet adhesive composition renders the carpets impervious to water so that soil and stains may be washed from the carpet without wetting the carpet underpad.

10 In order to maintain the aesthetic appearance of carpets, it is necessary to clean them periodically. The stain-resist properties of polyamide carpets that have been prepared using the stain-resist compositions and procedures referenced above may be degraded when the carpet is cleaned
15 with various detergents. When this occurs, the carpet is no longer sufficiently resistant to re-staining in the areas where washing has occurred, and subsequent stains resulting from spills containing acid-dyestuffs will leave a stained area that cannot be completely cleaned, leaving
20 an undesirable visible stain. In some instances, this problem may be overcome by applying more stain-resist composition to the carpet pile in the initial treatment process. However, this may lead to yellowing problems with certain stain-resist compositions upon exposure of the
25 treated carpet to nitrogen oxides or ultraviolet radiation due to the increased amount of stain-resist compositions on the carpet pile. Further, this increase in the amount of stain-resist agent used to treat the carpet can lead to effluent-treatment problems due to the increased amount of
30 stain-resist chemicals remaining in the used treatment bath. Alternatively, the afterwash stain performance of the carpet can also be improved by topically applying a stainblocker to the installed carpet as taught by Vinod in
35 U.S. Patent 4,925,707 or by Moore et al. in U.S. Patent 4,908,149. Such processes, however, may be expensive for

the carpet owner, and the results can be variable depending on the application methods used.

SUMMARY OF THE INVENTION

5 The present invention provides stain-resistant polyamide carpets which exhibit improved stain-resist performance after washing with a detergent, through addition of a stain-resist composition to the adhesive used to anchor the carpet tufts in the primary backing. The
10 present invention also makes it possible to apply less of the stain-resist composition to the carpet pile than is normally required. In some instances, the stain-resist agent may be applied to the carpet pile under milder pH conditions than would have been necessary to achieve
15 acceptable afterwash performance when using standard adhesives that do not contain a stain-resist composition, thus increasing the life of the equipment used to apply the stain-resist compositions.

 It has also been found that the present invention
20 increases the "tuft-bind" which is the term used to describe the force necessary to completely remove a yarn tuft from the carpet. The invention, therefore, serves to more securely anchor the carpet yarns into the primary backing.

25 DETAILED DESCRIPTION OF THE INVENTION

 The carpets of the current invention are constructed using methods well known in the art, except that a modified adhesive composition containing a stain-resist composition is used. A typical tufted carpet has a
30 primary backing of polypropylene or jute which may be woven or nonwoven, stitched with tufts which generally are loops and/or cut loops of polyamide carpet yarn which extend upward from the backing to form the carpet pile. The
35 underside of the primary backing is coated with an adhesive composition which serves to anchor the tufts in the primary

backing. The carpet pile may be comprised exclusively of polyamide yarns or of polyamide-blend yarns in which polyamide fibers are blended with fibers of one or more other types commonly used in carpeting, i.e. wool, polypropylene, acrylic, etc. A secondary backing of woven jute or polypropylene is usually applied to the underside of the carpet following application of the adhesive. The adhesive typically is a latex emulsion, which is dried and heated in a separate curing step. Normally the weight of the dry latex as applied to the carpet ranges from about 20-32 ounces/square yard ($0.68-1.05 \text{ kg/m}^2$), with 24 ounces/sq. yard (0.81 kg/m^2) being most common. The carpet is typically installed with an underpad between the floor and the carpet. Alternately, a foam may be applied to the primary backing which serves to anchor the tufts as well as to replace the secondary backing and padding. According to the current invention, an adhesive is considered to be any composition which is used to anchor the carpet tufts in the primary backing. Examples include the latex emulsions and foam compositions described above. The specific adhesive used depends on the type of carpet construction and end use (for example, residential, commercial, carpet tile, automotive carpet, etc.).

Examples of adhesive compositions which may be used in the present invention comprise latex emulsions which are known in the art for binding tufts of fiber in primary carpet backings. Examples of adhesive polymers useful in these emulsions are disclosed in Ucci U.S. Patent No. 4,579,762 and include, but are not limited to, polyvinyl acetates, polyacrylates, ethylene-vinylacetate copolymers, styrene-butadiene copolymers and carboxy styrene-butadiene copolymers. Typical foams include urethane and latex compositions.

The amount of stain-resist agent required in the

adhesive composition to provide a carpet having improved afterwash performance will depend on the particular stain-resist composition being used. It will also depend on the nature of the carpet pile fibers, including the specific polyamide polymer, the type of heatsetting process used, the amount of stain-resist composition originally on the carpet pile and the process used to apply the stain-resist agent to the carpet pile fibers. The same stain-resist agent that was used to treat the carpet pile fibers may be used in the adhesive. Alternatively, a different stain-resist agent may instead be used.

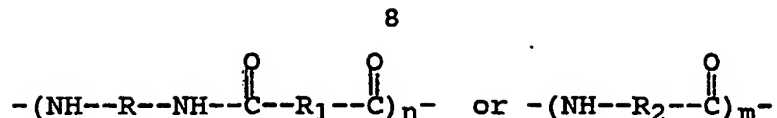
In a preferred aspect of the invention, the latex contains from 0.04 to 3.0 weight percent of the active stain-resist agent, the agents typically being supplied in the trade in the form of aqueous stain-resist compositions having concentrations from 20-30%. It is most preferred to use compositions containing from 0.04 weight percent to 0.9 weight percent of the stain-resist agent based on the weight of the latex.

The stain-resist agents are polymeric in nature and are either condensation polymers, addition polymers derived from one or more monomers having ethylenic carbon-carbon unsaturation, or mixtures of such condensation and addition polymers. Generally, the condensation polymers are derived from formaldehyde and either a sulfonated phenol or a sulfonated naphthol, and preferably a monosulfonated phenol. Generally, the addition polymers contain repeating units derived from maleic acid or methacrylic acid and up to 70 weight percent of a comonomer having ethylenic unsaturation and containing from 2 to 20 carbon atoms. More specifically, they include those such as the type described in EPO Publication No. 0329899, published August 30, 1989, or in the aforementioned U.S. Patent No. 4,883,839 to Fitzgerald et

al., the disclosure of each of which is incorporated herein by reference. These polymers contain repeating units derived from a hydrolyzed polymer of maleic acid and one or
5 more ethylenically unsaturated aromatic comonomers. Examples of such comonomers are styrene, alphanaphthyl styrene, and stilbene. The maleic acid generally is derived from maleic anhydride, that is, maleic anhydride is polymerized to form either a homopolymer or a copolymer
10 such as with styrene. The polymerized maleic anhydride can be hydrolyzed to maleic acid which, in turn, can be partially or wholly converted to its stereoisomer fumaric acid, such as by treating at an elevated temperature. Other types of addition polymers include those of the type
15 disclosed in the aforementioned EPO Published Application 332,342 to Chang et al. and U.S. Patent 4,822,373 to Olson et al., each of which is also incorporated herein by reference. Examples of these include the homopolymer polymethacrylic acid and copolymers of methacrylic acid
20 with up to 70 weight percent of an ethylenically unsaturated monomer such as alkyl acrylates having 1-4 carbon atoms, itaconic acid, and sodium sulfostyrene. The alkali metal salts of both the condensation and addition polymers may also, of course, be used.

25 Additionally a soil-resist composition may also be added to the adhesive in combination with the stain-resist. Generally, the soil-resist compositions contain organic compounds having a plurality of fluorine atoms which tend to repel foreign materials, i.e., soil. Soil-resist
30 compositions may also, of course, be topically applied to the fibers in the tufts in the conventional manner.

 The polyamides used to form the fibers in the tufts are aliphatic or cycloaliphatic in nature.
35 Generally, they have the formula



5 where -R-, -R₁-, and -R₂- are divalent aliphatic or cycloaliphatic radicals containing 4 to 20 carbon atoms. Such polyamides include polyhexamethylene adipamide, polyhexamethylene dodecamide, polycaprolactam, 6,6/6 copolyamide, polyaminoundecanoic acid, etc. The subscripts
10 n and m represent integers large enough to ensure fiber forming characteristics of the polyamide. Generally, the number average molecular weight of the polymer will be from 10,000 to 500,000.

In typical stain-resistant carpets made with
15 standard, unmodified latex adhesives, stain-resist compositions containing from as little as 0.2 to as much 1.5 weight percent active stain-resist agent (on weight of fiber) are directly applied to the fibers in the tufts to provide satisfactory stain-resistance both before and after
20 washing. The amount actually used will, of course, vary depending on such factors as the specific stain-resist being applied, the fiber polymer, heat-setting method, pH and other application conditions. By use of the modified latex compositions described herein, comparable performance
25 can be achieved with as much as about 10% less stain-resist, i.e. by treating the carpet pile with about 0.18 to 1.35 wt.% of the active agent.

Test Methods

In the test procedures and examples described
30 below, all percentages are by weight unless otherwise indicated.

Stain Test 1

Stain Test 1 used herein consists of two parts:
35 1) a 24 hour stain test on "As Is", i.e. tufted, dyed, and latexed, but unwashed carpet; and 2) a 24 hour stain test

on a carpet which has been subjected to a wash prior to staining (referred to as "After Wash"). The staining agent for both the "As Is" and "After Wash" evaluations is a solution containing 0.054 g/l of Red Dye No. 40 prepared from commercially-sold, cherry-flavored, sugar-sweetened "Kool-Aid" premix. The solution is made by dissolving 45 grams of this "Kool-Aid" premix powder in 500 ml of water, and it is allowed to reach room temperature, i.e., 75°F ($\pm 5^\circ\text{F}$) or 24°C ($\pm 3^\circ\text{C}$), before using.

"As Is" Evaluation

For the "As Is" evaluation, a carpet sample tufted from approximately 15 grams of fiber is prepared. Half of this sample is immersed in 40 cm³ of the staining agent. The staining agent is worked into the tufts for uniform staining. The sample is then placed on a flat non-absorbent tray or surface. The sample is left undisturbed for 24 hours (± 4). Then the stained sample is rinsed thoroughly with cool tap water, extracted to remove excess liquid, and dried.

The stain resistance of the carpet is visually determined by the amount of color left in the stained area of the carpet. This is referred to as the stain rating, and is herein determined according to the Stain Rating Scale (a copy of which is currently used by and available from the Flooring Systems Division of E.I. du Pont de Nemours and Company, Wilmington, DE 19898). These colors can be categorized according to the following standards:

- 5 = no staining
- 4 = slight staining
- 3 = moderate staining
- 2 = considerable staining
- 1 = heavy staining

In other words, a stain-rating of 5 is excellent, indicating good stain-resistance, whereas 1 is a poor

rating, indicating persistence of heavy staining.

"After Wash" Evaluation

For the "After Wash" evaluation, a 15 gram sample
5 of carpet is prepared. A detergent solution is made by
adding 57 grams of "Dupanol WAQE", an aqueous composition
containing about 30 weight percent of a surfactant made by
neutralizing the reaction product of chlorosulfonic acid
and lauryl alcohol (predominantly sodium lauryl sulfonate),
10 to 3.8 liters of water and adjusting the pH to 10.0 with an
aqueous solution of about 0.2% trisodium phosphate, and
allowing the solution to reach room temperature, i.e., 75°F
($\pm 5^\circ$) or 24°C ($\pm 3^\circ$), before using. The carpet sample is
completely immersed in the detergent solution for 5
15 minutes, the detergent solution being discarded after each
wash. Then the sample is rinsed thoroughly with cool tap
water, extracted to remove excess liquid, and dried.

The staining agent is then applied and evaluated
in the same manner as described above in the "As Is"
20 evaluation.

For a carpet to be considered to have a
commercially acceptable level of stain-resistance, it
should have a rating of at least 4 on the above-described
Stain Rating Scale for both the "As Is" and "After Wash"
25 evaluations.

Stain Test 2

The procedure followed in Stain Test 2 is
identical to that described for Stain Test 1, both for "As
Is" and "After Wash" evaluation, except that a different
30 method is used for staining the carpet sample. Instead of
immersing half of the carpet sample in the staining agent,
the specimens are placed on a flat non-absorbent surface
and 20 ml of the staining agent is poured on each specimen
35 through a cylinder (1-1/2 to 2 inches (3.8 to 5.1 cm)
diameter) to form a 1-1/2 to 2 inch (3.8 to 5.1 cm)

circular stain. The cylinder is removed and the solution worked into the tufts for uniform staining. The samples are left undisturbed for 24 ± 4 hours, rinsed thoroughly with cool tap water, squeezed dry and an extractor used to remove excess solution.

Tuft-Bind Measurement

Tuft-bind is measured using ASTM D 1335.

EXAMPLE 1

BCF (bulked continuous filament) nylon 6,6 yarns of 1150 total denier and comprised of 68 filaments (of trilobal cross-section) were produced by a conventional process. Two of these yarns were plied and twisted to provide a yarn having a balanced twist of 3.5 turns per inch (tpi). The resulting yarn was then conventionally heat-set in a Superba heat-set apparatus at 270 degrees F (132°C). A cut pile tufted carpet was constructed from the heat set yarn to the following specifications: 40 oz/sq.yd. (1.36 kg/m^2), 3/4 inch (1.9 cm) pile height, 1/8 inch gauge (31.5 tufts/decimeter), 8 1/4 stitches per inch (3.25 stitches/cm). This carpet was dyed to a light blue shade using a Kusters "Fluidyer" on a continuous dye line. A conventional continuous dye process (at 400% wet pick up) and dye auxiliaries were used (color formula was the following and based on the weight of carpet: 0.0200% Tectilon Blue 4R-200 (C.I. Acid Blue 277), 0.0060% Tectilon Red 2B-200 (C.I. Acid Red 361), and 0.0045% Tectilon Orange 3G-200 (C.I. Acid Orange 156), pH = 6.0). After dyeing, the carpet was rinsed and extracted.

The carpet was then treated with a bath containing a stain-resist composition on a Kusters "Flex-Nip" dyeing apparatus. The specific stain-resist composition used was an aqueous mixture of a hydrolyzed styrene/maleic anhydride copolymer and a sulfonated phenol-formaldehyde condensate, as described in the previously referenced patent U.S.

4,883,839. (The molar ratio of the copolymer was 1:1 styrene:maleic anhydride, and the copolymer had a number average molecular weight of 1600). The stain-resist composition was 75.3 wt% of a 30 wt% solution of the styrene:maleic anhydride copolymer, 13.3 wt% of a 30 wt% solution of the phenol-formaldehyde condensate, and 11.4% of the anionic surfactant "Alkanol ND", which contains 45 wt% of the disodium salt of dodecyldiphenyl oxide disulfonic acid as its active ingredient. The bath was prepared by water dilution of the stain-resist composition to contain 5.4 wt% of the composition owf (on the weight of fiber) or 1.2% owf based on active ingredient of the hydrolyzed styrene/maleic anhydride copolymer, 0.22% owf based on active ingredient of the sulfonated phenol-formaldehyde condensation product, and 0.28% based on active ingredient owf of the anionic surfactant "Alkanol ND". The carpet sample was treated by adjusting the pH of the stain-resist bath to 2.3 using sulfamic acid. The bath was applied to the carpet samples in a Kusters "Flex-Nip" at about 80 degrees F (26.7°C) and 400% wet pick-up on weight of fiber, followed by steaming in a vertical steamer for a residence time of 3 minutes. After the steamer, the carpet was rinsed and extracted. The carpet was subsequently treated with a commercial fluorochemical in a conventional spray application and the carpet was dried in an oven. This carpet sample is designated as Sample A.

Additional carpet samples were processed using the same procedure as for Sample A except that the pH was adjusted to 3.0, 3.5, and 4.0. These samples are referred to as Samples B, C, and D respectively.

A commercially available styrene-butadiene latex composition (Latex-V 9370 made by Colloids Inc., 207 Telegraph Ave. Gastonia, N.C. 28054) was hand applied to sections of the carpet samples A-D and the carpets were

13

oven-cured at 250 degrees F (121°C) for 5-7 minutes. Another set of samples was prepared using carpet Samples A-D except that the latex composition was modified to contain 1 wt% on the weight of latex (owl) of the same stain-resist solution that was applied to the carpet pile. In terms of the nonaqueous components, this corresponds to 0.23 wt% owl of the styrene-maleic anhydride copolymer, 0.04 wt% owl of the phenol-formaldehyde condensate, and 0.05 wt% owl of the anionic surfactant, with the copolymer and the condensation product being considered as the active ingredients of the stain resist solution. This stain-resist composition was added to the latex while stirring slowly for about 5 minutes using a Gifford Wood mixer, Model 76-IL, made by J. W. Greer, Inc. The modified latex, which contained the stain-resist composition, was hand applied to the carpet and oven-cured using the same conditions as described above. This set of carpet samples is designated by sample numbers A' - D' in TABLE 1 below. The dried latex weight on the carpet both for these samples and for all the carpets described in these Examples was approximately 30 oz/sq.yd. (1.02 kg/m²). The carpet was tested for stain resistance by Stain Test 2. The results from the Table 1 show that the samples with modified latex containing the stain-resist composition exhibited improved "after wash" stain performance versus samples with standard latex for all the samples regardless of the application pH of the stain-resist composition. The "as is" performance was almost equal for all the samples. This demonstrates that it is possible to apply the stain-resist composition to the carpets at a higher pH (i.e. milder conditions) and to achieve acceptable afterwash performance through the addition of stain-resist to the latex.

35

TABLE 1

Sample No.	Bath Application pH	Latex	Stain Rating	
			As Is	After Wash
5 A	2.3	STANDARD	5	4-5
A'	2.3	MODIFIED	5	5
B	3.0	STANDARD	4-5	3-4
10 B'	3.0	MODIFIED	5	4-5
C	3.5	STANDARD	4-5	4
C'	3.5	MODIFIED	4-5	4-5
15 D	4.0	STANDARD	5	3
D'	4.0	MODIFIED	5	4-5

EXAMPLE 2

20 The dyed carpet and the stain-resist composition as described in Example 1 were used for this experiment. Two samples were prepared, one at 4.5% owf and the other at 3.75% owf of the stain-resist composition, and are designated as Samples E and F, respectively. The stain-resist bath was adjusted to a pH of 2.3 with sulfamic acid. The samples were

25 finished with the standard latex and also with the modified latex containing 1% owl of the stain-resist composition as described in Example 1. These samples are referred to as Samples E' and F' in TABLE 2 below. The samples were tested using Stain Test 2. This example demonstrates that the use of

30 the stain-resist composition in the latex improves the staining performance for the samples which are processed with less stain-resist composition applied to the carpet pile.

TABLE 2

Sample No.	% Stain Resist Composition in Bath. (owf)	Latex	Stain Rating	
			As Is	After Wash
E	4.5	STANDARD	4-5	4-5
E'	4.5	MODIFIED	5	4-5
F	3.75	STANDARD	4-5	4
F'	3.75	MODIFIED	5	4-5

EXAMPLE 3

A mill-processed carpet sample was used in this example. The carpet was made from a BCF nylon 6,6 yarn of 1410 total denier. Two of these yarns were plied and twisted to provide a yarn having a balanced twist of 4.0 tpi. The resulting yarn was then heat-set in a Superba heat-set apparatus with stuffer box attachment at 270 degrees F (132°C). A cut-pile tufted carpet was constructed from the heat-set yarn to the following specification: 28 oz/sq.yd. (0.94 kg/m²), 3/4 inch (1.9 cm) pile height, 3/16 inch gauge (21 tufts/decimeter), 7.8 stitches per inch (3.07 stitches/cm). This carpet was dyed to an off-white color using levelling acid dyes on a Kusters continuous dye line. The carpet was then treated in a Kusters "Flex-Nip" with 6.0% owf of the same stain-resist composition as described in the Example 1, except that the composition did not contain the "Alkanol ND" surfactant. The stain resist composition was applied at a pH of approximately 2.25.

Different samples of this carpet were then hand coated with the unmodified standard latex of Example 1 and the modified latex containing 1.0% owl of the same stain-resist composition as described in Example 1. The stain performance of the samples was evaluated using Stain

16

Test 1 and the stain test results are reported in Table 3 below. The results show that the afterwash stain performance of the commercially processed mill samples is improved when the samples are finished with the modified latex composition.

TABLE 3

Latex	Stain Rating	
	As Is	After Wash
STANDARD LATEX	5	3
MODIFIED LATEX	5	4-5

EXAMPLE 4

The same dyed and stain-resist treated carpet samples as described in above Example 3 were used in this example. In addition to using the modified latex of example 3, two further modified latex compositions were used for this experiment. The first comprised the commercial latex used in previous examples and 1 wt% owl of a combined stain and soil resist composition, identified as SRC-1. SRC-1 contains 8.72 wt% based on active ingredient of the hydrolyzed styrene/maleic anhydride copolymer, 1.74 wt% based on active ingredient of the sulfonated phenol formaldehyde condensate and 3.8 wt% based on active ingredient of "Teflon" MF (a 30% active, anionic fluorochemical commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE). The second modified latex contained the commercial latex and 1% owl of the "Teflon" MF fluorochemical composition.

The carpet samples were hand latexed, oven-cured and then stain tested according to Stain Test 1. The results show that the afterwash stain improvement is greatest where the latex is modified with the stain-resist

17

composition alone, followed by the one where the latex contains both stain resist and soil resist (fluoro-chemical). The sample where the latex is modified with the soil-resist chemical (fluorochemical) alone did not improve the afterwash stain performance.

TABLE 4

10	Latex	Stain Rating	
		As Is	After Wash
	STANDARD LATEX	5	3
	MODIFIED LATEX	5	4-5
	LATEX + 1% SRC-1	5	4
15	LATEX + 1% "Teflon" MF	5	2-3

EXAMPLE 5

The dyed BCF carpet sample tufted from Superba-set yarns as described in Example 1 was used in this example, except the carpet was not treated with a stain-resist composition. One sample was prepared with the standard latex and four others were prepared with modified latex. The latex of each of these samples was modified to contain between 1% to 10% owl of the same stain-resist composition as that used for Example 3 (referred to as SRC-2 for identification purpose below). Viewing both the styrene-maleic anhydride copolymer and the condensation product as active ingredients, the addition of 1%, 3%, 5%, and 10% owl of this composition corresponds to the addition of 0.27 wt%, 0.81 wt%, 1.35 wt%, and 2.7 wt% respectively of the active components. Another sample was prepared with the standard latex to which was added 3 wt% owl of a solution containing 30 wt% active ingredient of a sulfonated phenolic formaldehyde condensate type stain-resist composition (referred to as SRC-3 for

18

identification purpose below), i.e. 0.9 wt% owl of the condensation product itself. A jute secondary backing was applied to all the samples after the latex coating. The samples were then stain-tested using Stain Test 1. The results reported in Table 5 below show that there is no appreciable afterwash stain improvement until the modified latex contained 10% owl of the stain-resist composition SRC-2. Even then, the sample showed some visible stain (stain-rating of 3). However, it is surprising that it is possible to impart some degree of stain-resistance to a carpet pile that has not been treated with a stain-resist agent simply by incorporating a stain-resist agent in the latex adhesive.

15

TABLE 5

Product	Stain Rating	
	As Is	After Wash
Standard Latex	1	1
Latex + 1% SRC-2	1	1
Latex + 3% SRC-2	1	1-2
Latex + 5% SRC-2	1	1-2
Latex + 10% SRC-2	1-2	3
Latex + 3% SRC-3	1	1

25

EXAMPLE 6

A mill-processed carpet sample made from 4.5 denier, unheatset nylon 6,6 staple was used in this example. The carpet had the following construction: 16 oz/sq.yd. (0.54 kg/m²), 1/10 inch gauge (39.4 tufts/decimeter) and 1/4 inch (0.64 cm) pile height. The carpet was dyed to a light yellowish beige color in a beck dyeing process using premetallized dyes. One sample was prepared by using a standard latex while others were prepared with a modified latex containing varying percentages of a stain-resist composition. All samples

35

were hand latexed, and oven-cured, after which a jute backing was applied. The stain-resist compositions added to the latex were SRC-2 and SRC-3, as previously described in Example 5. The SRC-2 concentration was varied between 1 wt% and 5 wt% owl, while SRC-3 was used at 3 wt% owl. All the samples were then stain tested using Stain Test 1. The results reported in Table 6 below show that there is a marginal improvement in the afterwash performance for the latex samples containing the stain-resist composition SRC-2 at 5% owl addition (1.35 wt% owl of the active components) and at 3% owl (0.9 wt% owl of the active component) of stain-resist composition SRC-3.

15

TABLE 6

Product	Stain Rating	
	As Is	After Wash
Standard Latex	1	1
Latex + 1% SRC-A	1	1-2
Latex + 3% SRC-A	1-2	1-2
Latex + 5% SRC-A	1-2	3
Latex + 3% SRC-B	2	3-4

Examples 5 and 6 demonstrate that the degree of improvement in afterwash stain performance depends upon the nature (i.e. the dye rate) of the pile yarn used. The Superba-set yarn, being more open in structure, has a higher dye rate than unheatset yarn, and thus is more susceptible to staining. Thus, the Superba-set yarn requires that more of the stain-resist agent be used in order to achieve a specified level of stain performance. Similarly, it is known that Suessen-set yarn is less susceptible to staining than Superba-set yarn. It can therefore be expected that less stain-resist agent would be required for effective results on carpets tufted from Suessen-set yarns. Since it is also known that nylon 6,6

20

is less vulnerable to staining than other polyamides such as nylon 6, it can be expected that adjustments in the amount of stain-resist agent added to the latex will be required depending on the specific polymer type in the fiber.

EXAMPLE 7

The dyed carpet as described in the Example 1 was used for this experiment. The carpet was treated in a Kuester's "Flex-Nip" with 6.0% owf (1.62 wt% active components) of the same stain resist composition as described in Example 1, except that it did not contain the "Alkanol ND" surfactant. The stain resist composition was applied at a pH of approximately 2.5. The samples were finished with the standard latex and also with modified latex compositions containing 2% owl of three stain-resist compositions used commercially. Each of these stain-resist compositions is chemically different from one another as outlined in different patents. The samples, identified as A (standard latex), and B, C, and D (modified latex), were then tested using Stain Test 1. The results reported in Table 7 below show that the afterwash stain performance is improved with the modified latex regardless of the type of the stain resist composition.

25

30

35

TABLE 7

	Sample No.	Latex	Stain Rating	
			As Is	After Wash
5	A	Standard	5	4
	B	Modified with same stain resist composition used to treat carpet pile of Example 7	5	5
10	C	Modified with the stain resist composition SRC-3 as described in Example 5	5	4-5
15	D	Modified to contain FX-661, a 25% active stain resist composition available from 3M Co.	5	5

EXAMPLE 8

A carpet prepared and dyed as described in Example 1 was treated in a Kuester's "Flex-Nip" with a 5.0 % owf of a stain-resist composition, identified as SRC-4, at a pH of approximately 2.5. The SRC-4 stain-resist composition was a 25% active solution of the sodium salt of a hydrolyzed styrene-maleic anhydride copolymer of the type described in EPO Publication No. 0329899, published August 30, 1989.

Samples were finished both with a standard latex and also with modified latex compositions containing 1.0, 2.0, and 3.0 % owl of two different stain-resist agents. Those were SRC-4, which is the same as that applied on the fiber, and the other one, identified as SRC-5, which is a nominal 30% active solution of "Mesitol" FC40556D, a sulfonated phenolic formaldehyde condensate product sold by Mobay Corporation. The samples were then stain tested using Stain Test 1 and evaluated for tuft-bind to determine the force required to pull a tuft completely out of each carpet

sample. The results reported in Table 8 below show that the "As Is" and the "After Wash" stain performance are both improved by the modified latex compositions, whether the modification is by SRC-4 or SRC-5. As might be expected, the results are best for 3.0%, followed by 2.0%, and then 1.0% owl for either of the stain resist compositions. When compared at equal percent addition of these stain resist compositions, the overall improvement was better with stain resist SRC-5 than with SRC-4. It can also be seen that the presence of stain-resist in the latex has the effect of more securely anchoring the tufts to the carpet's primary backing as all the samples made with the modified latexes had increased tuft-bind values versus that of Sample 1 which did not have stain-resist in the latex.

15

TABLE 8

Sample No.	Latex	As Is	Stain Rating After Wash	Tuft-Bind lbs. (kg)
1.	Standard	4-5	2	7.0 (3.2)
20 2.	Modified Latex with 1.0% owl of SRC-5	5	3	7.2 (3.3)
3.	Modified Latex with 2.0% owl of SRC-5	5	4	7.5 (3.4)
25 4.	Modified Latex with 3.0% owl of SRC-5	5	4-5	7.2 (3.3)
5.	Modified Latex with 1.0% owl of SRC-4	4-5	2-3	7.2 (3.3)
30 6.	Modified Latex with 2.0% owl of SRC-4	5	3	7.5 (3.4)
7.	Modified Latex with 3.0% owl of SRC-4	5	3-4	7.7 (3.5)

I CLAIM:

1. A fabric structure comprising a primary
5 backing stitched with closely spaced tufts of aliphatic
polyamide or polyamide-blend fibers which tufts extend
upwardly from the top surface of the primary backing to
form a pile, which fibers are coated with a polymeric
stain-resist composition, and which tufts are adhered to
10 the primary backing with an adhesive containing a polymeric
stain-resist composition.

2. The fabric structure of claim 1 wherein the
polymeric stain-resist composition in the adhesive adhering
the tufts to the primary backing comprises an active
15 polymeric stain-resist agent selected from the group
consisting of a sulfonated naphthol-formaldehyde
condensation product, a sulfonated phenol-formaldehyde
condensation product, a polymer of methacrylic acid or its
alkali metal salts, and up to 70 weight percent of one or
20 more monomers having ethylenic unsaturation and containing
from 2 to 20 carbon atoms, a polymer of maleic acid or
fumaric acid, or alkali metal salts thereof, and up to 70
weight percent of an ethylenically unsaturated aromatic
comonomer containing 2 to 20 carbon atoms, and mixtures
25 thereof.

3. The fabric structure of claim 2 wherein the
polymeric stain-resistant composition coated on the
aliphatic polyamide or polyamide-blend fibers comprises an
active polymeric stain-resist agent selected from the group
30 consisting of a sulfonated naphthol-formaldehyde
condensation product, a sulfonated phenol-formaldehyde
condensation product, a polymer of methacrylic acid, its
alkali metal salts, and up to 70 weight percent of one or
35 more monomers having ethylenic unsaturation and containing
from 2 to 20 carbon atoms, a polymer of maleic or fumaric

acid, or alkali metal salts thereof, and up to 70 weight percent of an ethylenically unsaturated aromatic comonomer containing 2 to 20 carbon atoms, and mixtures thereof.

- 5 4. The fabric of claim 3 wherein the polymeric stain-resist composition in the adhesive adhering the tufts to the primary backing contains from 0.04 to 3.0 weight percent of active polymeric stain-resist agent on the weight of the adhesive.
- 10 5. The fabric of claim 4 wherein the polymeric stain-resist composition coated on the fibers in the tufts comprises from about 0.18 to 1.35 weight percent of active stain-resist agent on the weight of the fibers in the tufts.
- 15 6. The fabric of claim 3 which is in the form of a carpet.
7. The carpet of claim 6 wherein the adhesive is a latex adhesive.
8. The carpet of claim 7 wherein the latex
20 contains an organic fluorochemical soil-resist composition.
9. The carpet of claim 7 wherein the stain-resist agent in the latex adhesive is a sulfonated phenolic formaldehyde condensate.
10. The carpet of claim 7 wherein the stain-
25 resist agent in the latex adhesive is a blend of a sulfonated phenolic formaldehyde condensate and a hydrolyzed styrene maleic anhydride copolymer.
11. The fabric of claim 5 which is in the form of a carpet.
- 30 12. The carpet of claim 11 wherein the adhesive is a latex adhesive.
13. The carpet of claim 12 wherein the latex contains an organic fluorochemical soil-resist composition.

25

14. The carpet of claim 12 wherein the stain-resist agent in the latex adhesive is a sulfonated phenolic formaldehyde condensate.

5 15. The carpet of claim 12 wherein the stain-resist agent in the latex adhesive is a blend of a sulfonated phenolic formaldehyde condensate and a hydrolyzed styrene maleic anhydride copolymer.

10

15

20

25

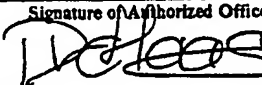
30

35

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/03969

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1.5 D 06 N 7/00 D 06 M 15/41		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.C1.5	D 06 N D 06 M	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,2129841- (SANDOZ) 23 May 1984, see the whole document	1-7
Y	---	8-15
Y	US,A,4643930 (UCCI) 17 February 1987, see the whole document -----	8-15
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
24-09-1991		15. 10. 91
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		 Danielle van der Haas

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9103969

SA 48488

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 09/10/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2129841	23-05-84	BE-A- 898135	03-05-84
		DE-A- 3338907	10-05-84
		FR-A, B 2535750	11-05-84
		JP-A- 59100783	11-06-84
		US-A- 4503191	05-03-85

US-A- 4643930	17-02-87	None	
